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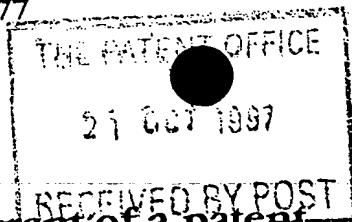
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Dated

29 October 1998



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P01/7700 25.00 - 9722102.2

# Request for grant of a patent

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The Patent Office

Cardiff Road  
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1. Your reference MEL-2,3-DISUB

2. Patent application number  
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21 OCT 1997

9722102.2

3. Full name, address and postcode of the or of each applicant (underline all surnames)

CAMBRIDGE DISPLAY TECHNOLOGY  
181a Huntingdon Road  
CAMBRIDGE CB3 0DJ  
(Reg. Office  
13 Station Road Cambridge CB1 2JB)

616644002

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

U.K. (GB)

4. Title of the invention

MATERIALS FOR POLYMER ELECTROLUMINESCENT DEVICES

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

from 51/77 21.10.97

Dr A.B. Holmes  
Melville Laboratory for Polymer Synthesis  
Pembroke Street  
CAMBRIDGE CB2 3RA

Page White & Farra  
54 Doughty Street  
LONDON  
WC1N 2LS

Patents ADP number (if you know it)

7038292002

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
  - b) there is an inventor who is not named as an applicant, or
  - c) any named applicant is a corporate body.
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Continuation sheets of this form

Description 12

Claim(s) J

Abstract

Drawing(s) 8 figures included in above 12 pages

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11. I/We request the grant of a patent on the basis of this application.

Signature

Andrew B. Holmes

Date 18 October 199

12. Name and daytime telephone number of person to contact in the United Kingdom
- Dr A B Holmes  
Tel: 01223 334370  
Fax: 01223 334866

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## MATERIALS FOR POLYMER ELECTROLUMINESCENT DEVICES

### References Cited

#### U.S. PATENT DOCUMENTS

3,401,152/1968 Wessling et al.

5,558,904 Hsieh et al.

5,189,136/1990 Wudl, F.

#### OTHER PUBLICATIONS

J. H. Burroughes et al., *Nature*, 1990, **365**, 47.

H. G. Gilch et al., *J. Polym. Sci. 1-A*, 1966, **4**, 1337.

B. R. Hsieh et al., *Adv. Mater.*, 1995, **7**, 36.

WO 95/32526 Staring & Demandt

H. Antoniadis et al., *Polym. Adv. Tech.*, 1997, **8**, 392

### SUMMARY

Organic materials-based light-emitting diodes (LEDs) are disclosed in which the use of a layer of emissive polymer enables efficient devices to be constructed using aluminium or calcium cathodes. The polymer, a poly(1,4-phenylene vinylene) (PPV) derivative, carries substituents on the 2,3-positions of the phenylene ring. This substitution pattern produces a blue-shifted emission and high PL and EL device efficiencies. The polymerisation route is simple, the polymer is soluble, and displays good film forming properties with high photoluminescence in the solid state.

## MATERIALS FOR POLYMER ELECTROLUMINESCENT DEVICES

### FIELD OF INVENTION

The present invention is directed to polymer-based light-emitting diodes (LEDs), in particular to the synthesis and fabrication of novel 2,3-disubstituted poly(1,4-phenylene vinylene) derivatives based LEDs.

## BACKGROUND OF INVENTION

The potentially high photoluminescent quantum yield in organic semiconductors has made light emission through charge injection under an applied field (electroluminescence) a reality. This has thus resulted in the use of organic materials for LEDs, with the use of polymers as an advantage over smaller organic compounds in improving structural stability and processibility of the organic layers.

The first polymer-based LEDs consisted of an emissive layer of poly(1,4-phenylene vinylene) (PPV) sandwiched between indium tin oxide (ITO) as the hole injection electrode and aluminium or calcium as the electron-injecting electrode (Burroughes et al., *Nature*, 1990, **347**, 539). This has been followed in other polymers for LED applications, with emphasis on the tuning of the emission colour by controlling the substitution pattern and the effective conjugation length in the polymer.

The route used for the synthesis of PPVs for LEDs has been predominantly the Wessling sulfonium salt precursor route (U.S. Pat. 3,401,152/1968 Wessling et al.) while another important method by Gilch (Gilch et al., *J. Polym. Sci. 1-A*, 1966, **4**, 1337), involved dehydrohalogenation of bis(halomethyl)benzene monomers with excess potassium *t*-butoxide to directly obtain the conjugated polymer. This protocol has been applied to the red emissive poly(2,5-dialkoxy-1,4-phenylene vinylene)s which have a typical absolute PL efficiency of ca. 15-20%. Most commonly the preparation has referred to poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (Wudl U.S. Pat. 5,189,136/1990). A modification of this route by Swatos and Gordon, based on the the chloro-precursor route, used one equivalent of base to form the chloro-substituted soluble precursor polymer which was then thermally converted to form the fully conjugated polymer [Swatos and Gordon, *Polym. Prepr.*, 1990, **31** (1), 505]. This route has since been used by various groups to make alkyl-, aryl- and alkoxy-substituted PPVs (Hsieh et al., *Adv.*

*Mater.*, 1995, 7, 36; *Polym. Adv. Tech.*, 1997, 8, 392; U.S. pat. 5,558,904; Sarnecki et al.; *Synth. Met.*, 1995, 69, 545).

#### SUMMARY OF THE INVENTION

The present invention describes the surprising discovery of efficient (relatively) blue-shifted emission from 2,3-disubstituted PPV-based materials and their use in LEDs. This invention explores the unconventional substitution patterns at the 2,3-positions on the aryl ring as opposed to the standard 2,5-disubstituted PPVs and thus provides a means of tuning the colour of emission. In addition, the present invention provides a luminescent polymer that is both soluble and directly obtainable by the Gilch route. The invention refers to the synthesis of novel materials and their application in organic LEDs.

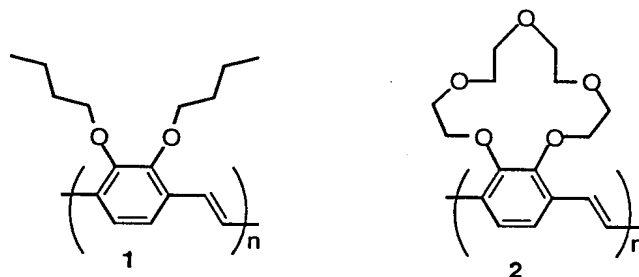
#### DESCRIPTION OF THE INVENTION

The electroluminescent (EL) device according to the present invention are injection-type diodes in which at least one active (EL) and one or more charge transport layers (if desired) are sandwiched between two different conducting layers (electrodes). One electrode is a hole-injecting translucent or transparent electrode while the other is an electron-injecting electrode. The electrodes are electrically connected to each other and to a source of current to create a complete circuit. Improved efficiencies may be obtained using bilayer devices with PPV or hole transporting layers e.g. poly(vinyl carbazole) (PVK).

This invention refers in one specific embodiment to the synthesis of the polymer, poly[(2,3-dibutoxy)-1,4-poly(phenylene vinylene)] **1** using the dehydrohalogenation method with base (potassium tert-butoxide). The resultant polymer has high molecular weight and its alkyl chains enable solubility in organic solvents such as chloroform and

tetrachoroethane. Surprisingly, the solid film fluoresces with high efficiency (absolute PL efficiency 40%) in the yellow green region despite having alkoxy substituents. In a further example the polymer **2** was synthesised. In addition to its emissive properties in PL and EL devices it has the potential to serve as a component of a sensor owing to its affinity for metal ions.

In a further embodiment, the fluorescent oligomer **9** has been synthesised using the Wadsworth-Emmons reaction of a dialkoxybenzyl bisphosphonate **8** and dialkoxy-benzaldehyde **7**. Evidence for the origin of the blue shifted emission and possible high fluorescence efficiency comes from the single crystal X-ray study of **9** which shows that the aromatic rings are twisted in a notable manner, thus resulting in the disruption of the effective conjugation length of the polymer backbone. The localisation of the conjugation could also be due to the cisoid-like disposition of the styryl substituents in **9**. (see Figure 4 later)



**Figure 1** Structure of the poly[(2,3-dibutoxy)-1,4-poly(phenylene vinylene)] (PDB-PPV) **1** and the crown ether analogue **2**

Two layer devices were fabricated using **1** as follows. A layer of a PPV precursor polymer, fabricated according to the sulfonium salt decomposition method described in U.S. Patent No. 3,401,152/1968, is spin-coated onto a glass plate coated with ITO and thermally converted to PPV. In the other type of bilayer device, a transporting layer of PVK is spin-coated from solution directly onto ITO.



Next, a layer of the polymer poly[(2,3-dibutoxy)-1,4-poly(phenylene vinylene)] (PDB-PPV) 1 is spin-coated onto the PPV layer followed by a layer of aluminium or calcium deposited under vacuum onto the polymer layer. Contacts are attached and a connection is made to a DC power source. Application of a forward bias voltage results in emission of yellow-green light with emission maximum at about 2.3 eV (ca. 550 nm), and a brightness in excess of 4,500 cd/m<sup>2</sup>. Internal efficiencies of about 1.5% were observed with calcium as the cathode.

Based on the illustrative examples it is evident that highly efficient devices can be obtained by the dehydrohalogenation route to prepare 2,3-disubstituted-1,4-arylenevinylene polymers from monomers carrying aryl, heteroaryl, alkyl, and branched alkyl substituents linked either by carbon or heteroatom linkages to the aromatic backbone of the polymer. Such substituents in the 2,3-positions could be selected from H, R, RO, RS, RR'N where R = C<sub>5</sub>H<sub>11</sub>, C<sub>6</sub>H<sub>13</sub>, C<sub>8</sub>H<sub>17</sub>, etc. and branched derivatives thereof, Ar where Ar = aryl or heteroaryl or fused derivatives thereof. Preferable substituents are those which solubilise the final polymer. These include branched alkyl, aralkyl and the corresponding alkoxy derivatives. The most preferred substituent is the butyloxy and other preferred substituents are ethylhexyl(oxy) and 3',7'-dimethyloctyl(oxy). Other carbon chains such as alkyl or alkoxy substituents carrying up to ten carbon atoms and branching substituents are advantageous. Such substituents could be selected in any combination, and are not limited to those listed. Similar effects are expected with any conjugated polyarylenevinylene polymer or other conjugated polymer (polyfluorene, polythienylene, polynaphthalene, polyphenylene, polypyridine, polyquinoline, polyquinoxaline, poly[thienylene-co-phenylene] etc) or a copolymer arising from a fluorescent unit carrying a distyrylbenzene fragment with the 2,3-disubstitution at least on the aromatic rings. The preferred polymers arise from poly(arylenevinylene) conjugated units carrying the 2,3-disubstitution pattern. Most preferably 2,3-disubstituted bishalomethylbenzene derivatives serve as starting monomers for the conjugate polymer products.

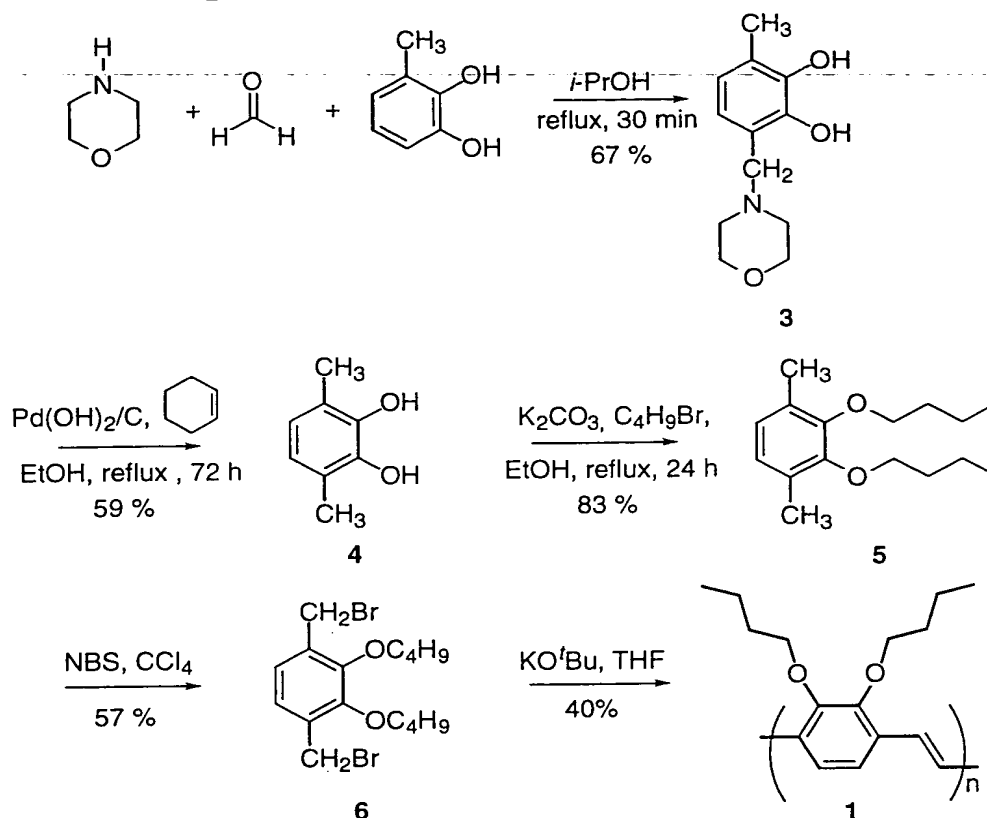
The preferred synthesis involves dehydrohalogenation condensation polymerisation using potassium t-butoxide as base in various solvents such as tetrahydrofuran or dioxane. The resulting polymer is solution processible and has a good film forming property for polymer electroluminescent devices.

Polymers from 1,4-bis(halomethylbenzene) monomers have been disclosed in U.S. pat. 5,558,904. These afforded insoluble polymers. The 2,3-disubstitution in the present invention is novel owing to the method of synthesis of the polymer, the fact that the product polymer is solution processible, and the surprising effect on the fluorescence emission wavelength and efficiency.

Previous examples with a 2,3-diphenyl (diaryl) substitution pattern as disclosed in U.S. pat. 5,558,904 would not be expected to demonstrate these novel features based on the lack of solubility of the final polymer as disclosed in detail in H. Antoniadis et al., *Polym. Adv. Tech.*, 1997, 8, 392. In that case solution processibility required the use of the precursor route to allow processing and generation of the final polymer.

#### EXAMPLES

A method of preparing the conjugated polymer PDB-PPV 1 involves the preparation of the monomer of formula  $\text{Br-CH}_2\text{-Ar-CH}_2\text{-Br}$  which is subjected to polymerisation with six equivalents of base, potassium tert-butoxide preferably in THF or dioxane to give the desired polymer which is soluble in organic solvents such as chloroform and tetrachloroethane. The synthesis of the polymer is shown in the following scheme (Fig 2):



**Figure 2** Preparation of PDB PPV 1

#### EXAMPLE 1 Preparation of monomer 6

Methyl catechol derivative 3 was synthesised by performing a Mannich reaction with formaldehyde and morpholine following the method described by Helgeson et al. (*J. Am. Chem. Soc.*, 1977, **99**, 6411). Transfer hydrogenation using palladium hydroxide on carbon to remove the morpholine group in the presence of a hydrogen donor (Hanessian et al., *Synthesis*, 1981, **118**, 396) subsequently produced the dimethyl catechol 4 in reasonable yield (59%). O-alkylation was then carried out using copious excess of potassium carbonate and dibutyl bromide to give a reasonably high yield (83%) dialkoxy-xylene 5. Radical bromination of the xylene with slight excess of *N*-bromosuccinimide in carbon tetrachloride as given in Gruter et

al., *J. Org. Chem.*, **59**, 4473 gave the monomer 6 in comparatively high yield (57%).

#### EXAMPLE 2 Preparation of polymer 1

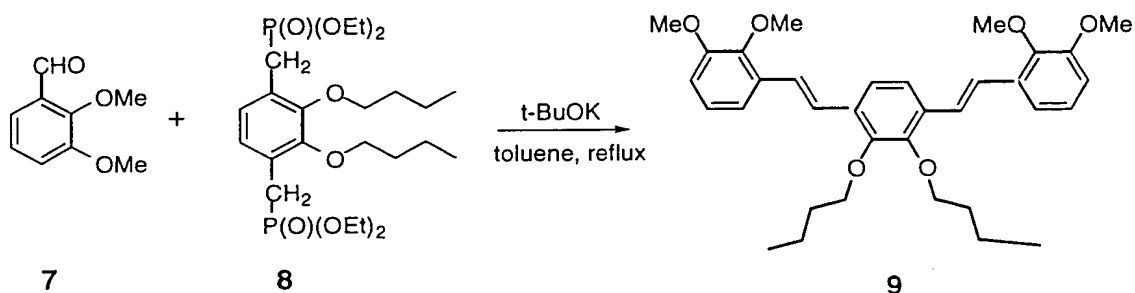
A degassed solution of the monomer 6 (0.24 g, 0.6 mmol) in dry THF (16 cm<sup>3</sup>) was added slowly over 20 min to a degassed solution of potassium tert-butoxide (0.41 g, 3.6 mmol) in dry THF (16 cm<sup>3</sup>) at room temperature. The reaction mixture was stirred at room temperature under nitrogen for 18 h, after which it was poured into methanol. The resultant yellow precipitate was collected by filtration and reprecipitated into methanol. The polymer (1) was collected as a bright yellow solid (60 mg, 40 %). Found: C, 76.6; H, 9.1; Br, 0 ; [C<sub>16</sub>H<sub>22</sub>O<sub>2</sub>]<sub>n</sub> requires C, 78.0; H, 9.0; Br, 0 %). GPC assay in CHCl<sub>3</sub> revealed  $M_w$  2,120,000,  $M_n$  361,000 and  $M_w/M_n$  5.9;  $\lambda_{max}(CHCl_3)/nm$  444;  $\lambda_{max}(film)/nm$  450; PL emission (max)/nm 551 (2.25 eV); PL efficiency 40 %; EL emission (max)/eV 2.28.

#### EXAMPLE 3 Fabrication of a 2-layer LED with polymer 1

A film of PPV (ca. 100 nm in thickness) was prepared by spin-coating a solution of a sulfonium precursor polymer onto a glass plate coated with indium tin oxide and thermally converting the film at 230 °C in vacuum for 6h. A 1% (w/v) solution of the polymer 1 in chloroform was spin-coated on top of the converted PPV film to give a uniform film of about 100 nm thick. The structures were placed on top of a mask, permitting the deposition of aluminium or calcium on the coated film surface inside a metal evaporator. Metal layers were of typically 500-1000 Å in thickness. Metal contacts were then attached to the electrodes and connected to a DC source. The active device area was typically 4 mm<sup>2</sup>.

The bilayer device (ITO/PPV/PDB-PPV/Ca) shows maximum efficiency 1.5 % with luminance in excess of 4,500 cd/m<sup>2</sup> with turn-on voltage at 9V. A bilayer device was also constructed with PVK as the hole-transporting layer produced a maximum efficiency of 0.6% with Al cathodes.

EXAMPLE 4 Preparation of the model oligomer 9



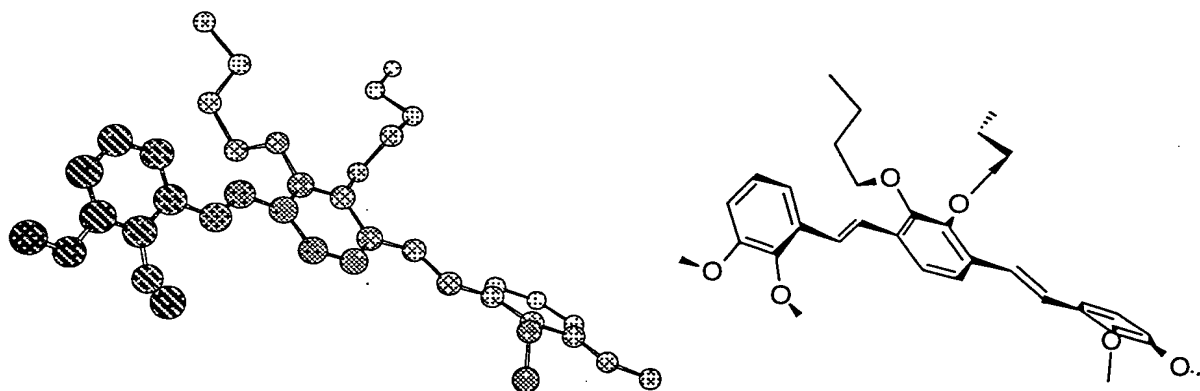
pale green crystals, m.p. 80-81 °C  
 $\lambda_{\text{max}}$  (CHCl<sub>3</sub>) 362 nm, (film) 366 nm  
 blue-green fluorescence, PL<sub>max</sub> (film) 2.6 eV

**Figure 3** Preparation of dialkoxy-substituted oligomer 9

A mixture of the 2,3-dimethoxybenzaldehyde **7** (0.33 g, 2.0 mmol) and 1,4-[(2,3-dibutoxy)xylylene]bis(diethylphosphonate) **8** (0.52 g, 1.0 mmol) in toluene (10 cm<sup>3</sup>) was stirred and heated to ca. 100 °C under an atmosphere of nitrogen. Potassium tert-butoxide (0.35 g, 3.0 mmol) was added all at once into the hot mixture resulting in a colour change to orange-brown. The mixture was then heated to reflux for 4 h. After allowing to cool to room temperature, toluene was added (20 cm<sup>3</sup>) followed by hydrolysis with acetic acid (10% aq, 20 cm<sup>3</sup>). The organic layer was separated, washed with water until the organic layer was tested neutral. The organic fraction was then dried, followed by removal of the solvent under reduced pressure to yield a yellow oil. The product **9** was isolated by column chromatography (99:1 hexane:diethyl ether v/v) and further purified by recrystallisation from methanol to give greenish-white needles (0.35 g, 64 %). m.p. 80.0-81.0 °C;  $\delta_{\text{H}}$  (250MHz; CDCl<sub>3</sub>) 7.49-7.47 (6H, m, Ar-H & CH=CH), 7.30-7.26 (2H, m, ArH<sub>a</sub>), 7.08 (2H, t, *J* 8.0, ArH<sub>b</sub>), 6.86-6.83 (2H, m, ArH<sub>c</sub>), 4.04 (4H, t, *J* 6.6, ArOCH<sub>2</sub>), 3.89-3.87 (12H, m, ArOCH<sub>3</sub>), 1.88-1.77 (4H, m, CH<sub>2</sub>), 1.64-1.49 (4H, m, CH<sub>2</sub>), 1.00 (6H, t, *J* 7.2, CH<sub>3</sub>);  $\delta_{\text{C}}$  (63.5 MHz; CDCl<sub>3</sub>) 153.1 (C, Ar), 150.6 (C, Ar), 147.1 (C, Ar), 132.0 (C, Ar), 131.7 (C,

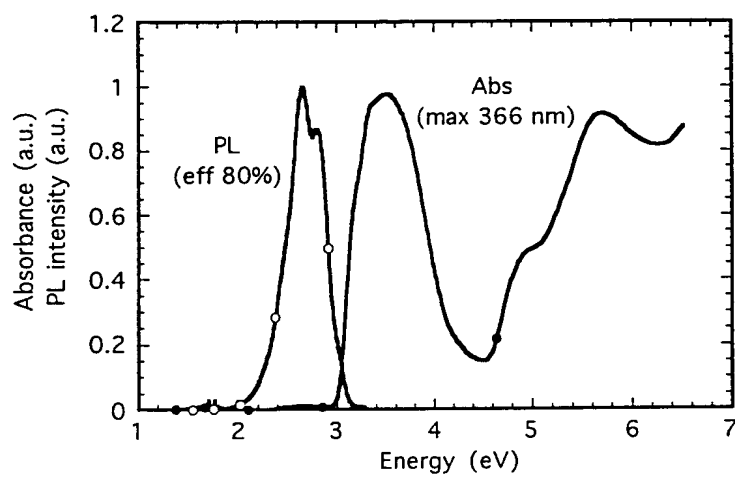
Ar), 124.2 (CH, Ar), 124.1 (CH, Ar), 123.4 (CH, Ar), 121.0 (CH, Ar), 117.9 (CH, Ar), 111.3 (CH, Ar), 73.7 (OCH<sub>2</sub>), 61.1 (OCH<sub>2</sub>), 55.8 (OCH<sub>2</sub>), 32.4 (CH<sub>2</sub>), 19.4 (CH<sub>2</sub>), 14.0 (CH<sub>3</sub>); *m/z* (CI) 547 (MH<sup>+</sup>, 75 %), 402 (10), 166 (40), 72 (C<sub>4</sub>H<sub>8</sub>O, 60), 52 (C<sub>4</sub>H<sub>4</sub>, 70); Found (MH<sup>+</sup>) 547.3060; C<sub>34</sub>H<sub>42</sub>O<sub>6</sub> requires 546.2981; (Found: C, 74.7; H, 7.8; C<sub>34</sub>H<sub>42</sub>O<sub>6</sub> requires C, 74.7; H, 7.8 %);  $\lambda_{\text{max}}$  (CHCl<sub>3</sub>/nm) 366;  $\lambda_{\text{max}}$  (film/nm) 362; PL<sub>max</sub> (film/nm) 477; PL efficiency (solid state) ca. 80%.

X-ray structure of **9**

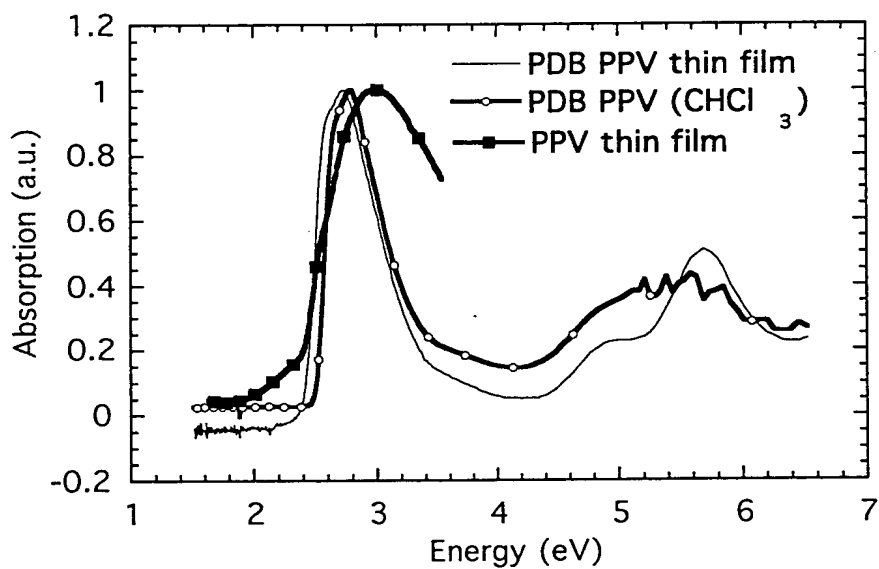


**Figure 4** The X-ray crystal structure of oligomer **9**

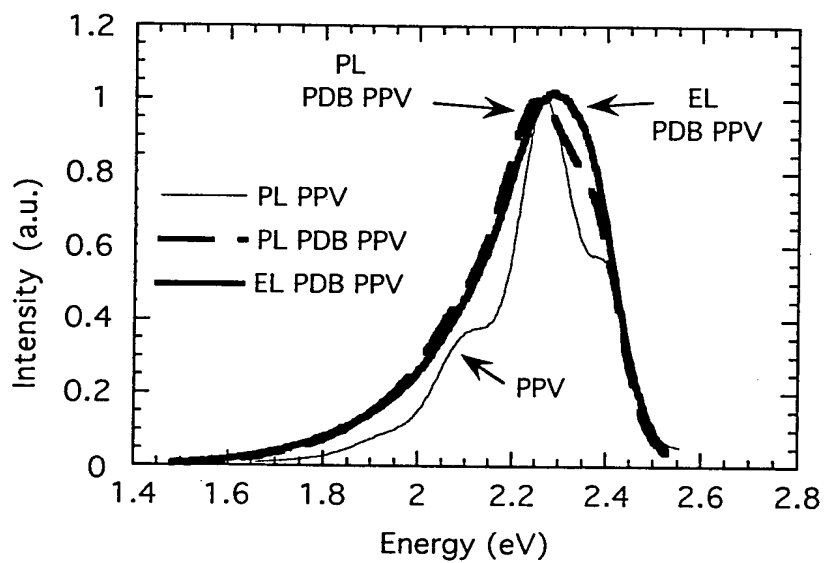
The X-ray of the oligomer **9** shows an unusual cisoid-like conformation around the *trans*-vinylene bond (Figure 4). The benzene rings are twisted out of the plane of the vinylene linkage by about 15° and the benzene rings in turn are twisted at a 30° angle from one another in a regular pattern. This twist will eventually cause an interruption in the polymer backbone conjugation after every 4 benzene rings. The oligomer shows high PL efficiency (ca. 80±8 %) in the solid state.



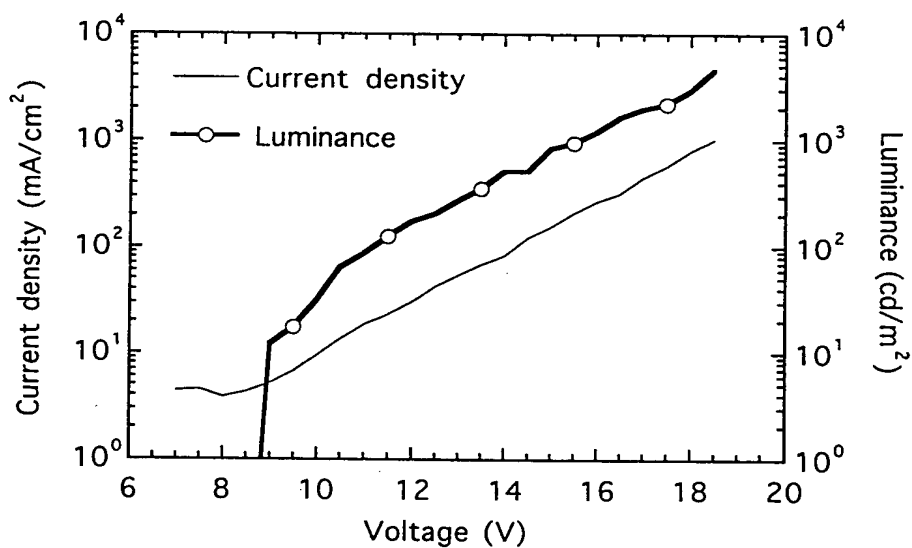
**Figure 5** Absorption and PL spectra of films of oligomer 9



**Figure 6** Absorption spectra of PDB PPV 1 compared with PPV film



**Figure 7** PL spectra of PDB PPV 1 compared with PPV film and EL spectra of a bilayer device (configuration ITO/PPV/PDB-PPV 1/Ca)



**Figure 8** Plot of current density vs applied voltage for a bilayer device (configuration ITO/PPV/PDB-PPV/Ca)